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JC09 Rec'd PCT/PTO 1 5 FEB 2001

FORM PTO-1390 DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE (REV 1-98)		ATTORNEY'S DOCKET NO. MIDR 704
<b>TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371</b>		U.S. APPLICATION NO. (If known, see 37 CFR 1.53) <b>09/763239</b>
INTERNATIONAL APPLICATION NO. PCT/GB99/02623	INTERNATIONAL FILING DATE 09 AUG 1999 (09.08.1999)	PRIORITY DATE CLAIMED 15 AUG 1998 (15.08.1998)
TITLE OF INVENTION SHALE-STABILIZING ADDITIVES		
APPLICANT(S) FOR DO/EO/US SMITH, Carl Keith; BALSTON, Terence George		
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:		
<ol style="list-style-type: none"><li><input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</li><li><input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.</li><li><input type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).</li><li><input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.</li><li><input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)).<ol style="list-style-type: none"><li><input checked="" type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau).</li><li><input checked="" type="checkbox"/> has been transmitted by the International Bureau.</li><li><input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</li></ol></li><li><input type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)).</li><li><input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).<ol style="list-style-type: none"><li><input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau).</li><li><input type="checkbox"/> have been transmitted by the International Bureau.</li><li><input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</li><li><input checked="" type="checkbox"/> have not been made and will not be made.</li></ol></li><li><input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</li><li><input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).</li><li><input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</li></ol>		
Items 11 to 16 below concern document(s) or information included:		
<ol style="list-style-type: none"><li><input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</li><li><input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</li><li><input checked="" type="checkbox"/> A <b>FIRST</b> preliminary amendment. <input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment.</li><li><input type="checkbox"/> A substitute specification.</li><li><input type="checkbox"/> A change of power of attorney and/or address letter.</li><li><input checked="" type="checkbox"/> Other items or information: Return Postcard, Application Data Sheet</li></ol>		

## CERTIFICATE OF EXPRESS MAILING

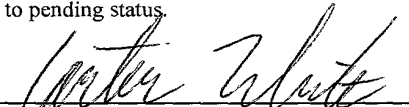
EL521287740US

NUMBER

DATE OF DEPOSIT February 15, 2001

I hereby certify that this paper or fee is being deposited with the United States Postal Service "EXPRESS MAIL POST OFFICE TO ADDRESSEE" service under 37 C.F.R. 1.10 on the date indicated above and is addressed to Assistant Commissioner for Patents, Washington, DC 20231

Barli Sofia  
Signature

U.S. APPLICATION NO. <b>097/765239</b> (known/see 37 CFR 1.5)		INTERNATIONAL APPLICATION NO. PCT/GB99/02623		ATTORNEY'S DOCKET NUMBER MIDR704	
17. <input checked="" type="checkbox"/> The following fees are submitted: <b>Basic National Fee (37 CFR 1.492(a)(1)-(5)):</b> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO ..... \$1000.00  International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ..... \$860.00  International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... \$710.00  international preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... \$690.00  International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) ..... \$ 100.00  <div style="text-align: right;"><b>ENTER APPROPRIATE BASIC FEE AMOUNT = \$1000.00</b></div>				<b>CALCULATIONS</b> PTO USE ONLY	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$130.00	
Claims	Number Filed	Number Extra	Rate		
Total Claims	11 - 20 =	0	x \$ 18.00	\$0.00	
Independent Claims	3 - 3 =	0	x \$ 80.00	\$0.00	
Multiple dependent claim(s) (if applicable)			+ \$270.00	\$0.00	
<b>TOTAL OF ABOVE CALCULATIONS =</b>				<b>\$1130.00</b>	
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (NOTE: 37 CFR 1.9, 1.27, 1.28)				\$ .00	
<b>SUBTOTAL =</b>				<b>\$1130.00</b>	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				+\$n/a.00	
<b>TOTAL NATIONAL FEE =</b>				<b>\$1130.00</b>	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property)				+\$ .00	
<b>TOTAL FEES ENCLOSED =</b>				<b>\$1130.00</b>	
				Amount to be refunded:	\$ .00
				charged	\$ .00
a. <input type="checkbox"/> A check in the amount of \$ _____.00 cover the above fees is enclosed. b. <input checked="" type="checkbox"/> Please charge my Deposit Account No. <u>01-2508/MIDR704</u> in the amount of \$ <u>1130.00</u> to cover the above fees. A duplicate copy of this sheet is enclosed. c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>01-2508/MIDR704</u> . A duplicate copy of this sheet is enclosed.  NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO:  Carter J. White, Patent Agent HOWREY SIMON ARNOLD & WHITE LLP 750 Bering Drive Houston, TX 77057-2198 (713) 787-1400			<div style="text-align: right;">  15 Feb 01         </div> SIGNATURE  Carter J. White, Patent Agent NAME  <u>41,374</u> REGISTRATION NUMBER		



27551

PATENT TRADEMARK OFFICE

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: SMITH, Carl K. et al.

Group Art Unit: Not Known

International Application No.: PCT/GB99/02623

Examiner: Not Assigned

Confirmation No.: Not Known

Atty. Dkt. No.: MIDR 704

International Filing Date: 09AUG 1999  
(09.08.1999)

For: SHALE-STABILIZING ADDITIVES

**First PRELIMINARY AMENDMENT**

Commissioner for Patents  
Washington, D.C. 20231

CERTIFICATE OF MAILING  
37 C.F.R. 1.8

I hereby certify that this correspondence is being deposited with the US  
Postal Service as First Class Mail in an envelope addressed to:  
Commissioner for Patents, Washington, D.C. 20231, on the date below:

Date

Signature

Before undertaking the examination of the above noted application,  
Applicants hereby request the following:

**AMENDMENTS:**

**IN THE SPECIFICATION:**

Please amend the specification in the following manner:

On page 1, line 1 of the specification, please insert the following text, -- This is a U.S.  
National Phase entry under 35 USC §371 of International Application No. PCT/GB99/02623,  
filed 09 AUG 1999 (09.08.1999) designating the US which claims priority to British Patent  
Application No. 9817780.1 filed 15 AUG 1998 (15.08.1998) the contents of both being herein  
incorporated by reference.--

**IN THE CLAIMS:**

Amended claims 1-11 are currently pending in the application. Please amend the claims  
in the following manner:

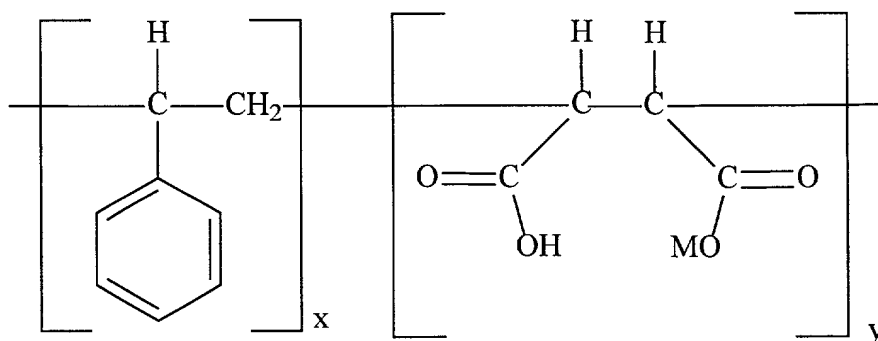
3. (Amended) The additive of claim 1 [or 2], wherein the polymer is a copolymer of styrene or a styrene derivative and maleic anhydride with alkylene oxide based side chains.

4. (Amended) The additives of [any one of claims 1 to 3] claim 1, wherein the polymer has a molecular weight of from 5000 g/mol to 100,000 g/mol.

5. (Amended) The additive of [any one of claim 1 to 4] claim 1, wherein the weight of the alkylene oxide based side chains is above 200 g/mol.

6. (Amended) The additive of [any one of claims 1 to 5] claim 1, wherein the number of alkoxyates in the polymer side chain is up to 60 units.

7. (Amended) The additive of [any one of claim 1 to 6] claim 1, wherein the polymer has the molecular structure:



wherein M in each occurrence independently is hydrogen or  $-\text{[CH}_2\text{-CHR-O]}_n\text{-CH}_3$  with R being  $\text{CH}_3$  or  $\text{CH}_2\text{-CH}_3$  or hydrogen, with the proviso that at least some of the radicals M have the meaning of  $-\text{[CH}_2\text{-CHR-O]}_n\text{-CH}_3$ , n is from 3 to 70, [preferably greater than 4 and less than 60], and x and y each independently are from 1 to 100.

\*\*\*\*\*

Please include claims 12-21, if not already present in the international application. Applicant's would like to bring to the Examiner's attention that claims 14, 15, 16, 17 and 18 have been amended below to remove the multiple, multiple dependencies present in the claims present in the international application.

12. A method of stabilizing shale in a subterranean formation comprising the step of injecting an additive into the formation comprising a polymer based on an olefinically unsaturated hydrocarbon with alkylene oxide based side chains.

13. The method of claim 12 wherein the polymer is a copolymer of an olefinically unsaturated hydrocarbon and an ethylenically unsaturated carboxylic acid, carboxylic acid salt or carboxylic acid anhydride with alkylene oxide based side chains.

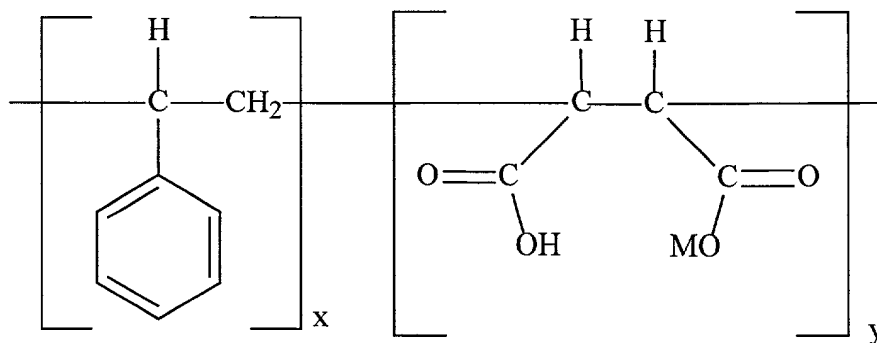
14. (Amended) The method of claim 12 [or 13], wherein the polymer is a copolymer of styrene derivative and maleic anhydride with alkylene oxide based side chains.

15. (Amended) The method of [any one of claim 12 to 14] claim 12, wherein the polymer has a molecular weight of from 5000 g / mol to 100,000 g/mol.

16. (Amended) The method of [any one of claim 12 to 15] claim 12, wherein the weight of the alkylene oxide based side chains is above 200 g/mol.

17. (Amended) The method of [any one of claim 12 to 16] claim 12, wherein the number of alkoxyates in the polymer side chain is up to 60 units.

18. (Amended) The method of [any one of claims 12 to 17] claim 12, wherein the polymer has the molecular structure:



wherein M in each occurrence independently is hydrogen or  $-\text{[CH}_2\text{-CHR-O]}_n\text{-CH}_3$  with R being  $\text{CH}_3$  or  $\text{CH}_2\text{-CH}_3$  or hydrogen, with the proviso that at least some of the radicals M have the meaning of  $-\text{[CH}_2\text{-CHR-O]}_n\text{-CH}_3$ , n is from 3 to 70, [preferably greater than 4 and less than 60,] and x and y each independently are from 1 to 100.

19. The method of claim 14, wherein the residual maleic anhydride groups in the polymer are hydrolyzed.

20. The method of claim 12 wherein the additive is added to a wellbore drilling or service fluid.

21. The method of claim 20 wherein the wellbore fluid is water based.

\*\*\*\*\*

**REMARKS:**

AMENDMENTS TO THE SPECIFICATION:

The above noted amendments to the specification have been made so as to properly present the priority claim and 35 USC §371 status information in order to claim priority.

Applicants' undersigned representative has enclosed a "redline" version of the specification indicating the above amendments for use by the Examiner. If for any reason there is a discrepancy between the amendments contained in this paper and the enclosed documents, Applicants request that the amendments of this paper be considered controlling.

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AMENDMENTS TO THE CLAIMS:

The above noted amendments to the claims have been made so that the scope and language of the claims is more precise and clear in defining what the Applicants consider to be his invention. Specifically, the claims as presented in the international application contain multiple, multiple dependencies have been removed from the claims which in order to bring such claims into conformance with US practice.

Applicants respectfully submit that no new matter is introduced by the proposed amendments to the specification. Applicants' undersigned representative has enclosed a complete set of the claims showing the changes desired. Enclosed is a full set of the amended claims in the condition desired after taking into account that above amendments as a courtesy to and a convenience for the Examiner. If for any reason there is a discrepancy between the

International Application No.: PCT/GB99/02623  
Confirmation No.: Not assigned  
Applicant: SMITH, Carl S. et al.  
Atty. Ref.: MIDR 704

The claims and amended claims are submitted as being clearly distinct and patentable over the art of record and therefore Applicants respectfully request their entry and allowance by the Examiner.

Applicants hereby request for any extension of time that may be deemed necessary to further the prosecution of this application. Applicants' representative hereby authorizes the Commissioner to charge any additional fees which may be required, or credit any overpayment, to Deposit Account No. 01-2508, referencing Order No. MIDR 704 .

In order to promote the prosecution of this application, the Examiner is hereby authorized to contact the undersigned by electronic mail. Please address all e-mail to: [whitec@howrey.com](mailto:whitec@howrey.com).

Carter White

Patent Agent

Tel. 713 268 1372

15 Feb '01

CLAIMS SHOWING AMENDMENTS OF: FEBRUARY 13, 2001

PAGE 1

WHAT IS CLAIMED IS:

1. An additive, when used as a shale stabilizer injected in subterranean formations, comprising a polymer based on an olefinically unsaturated hydrocarbon with alkylene oxide based side chains.

2. The additive of claim 1 wherein the polymer is a copolymer of an olefinically unsaturated hydrocarbon and an ethylenically unsaturated carboxylic acid, carboxylic acid salt or carboxylic acid anhydride with alkylene oxide based side chains.

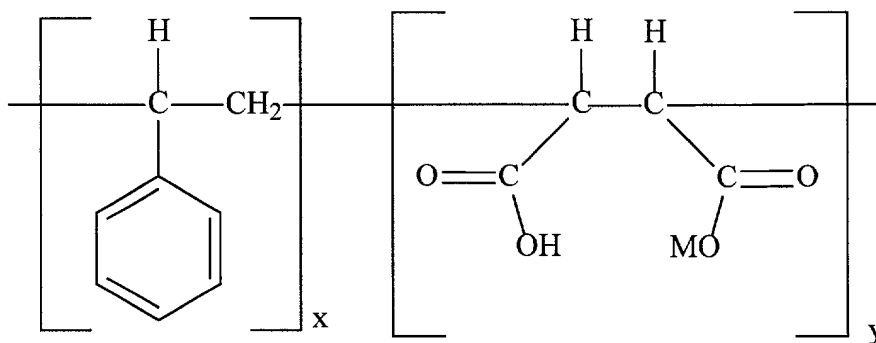
3. (Amended) The additive of claim 1 ~~or 2~~, wherein the polymer is a copolymer of styrene or a styrene derivative and maleic anhydride with alkylene oxide based side chains.

4. (Amended) The additives of ~~any one of claims 1 to 3~~ claim 1, wherein the polymer has a molecular weight of from 5000 g/mol to 100,000 g/mol.

5. (Amended) The additive of ~~any one of claim 1 to 4~~ claim 1, wherein the weight of the alkylene oxide based side chains is above 200 g/mol.

6. (Amended) The additive of ~~any one of claims 1 to 5~~ claim 1, wherein the number of alkoxylates in the polymer side chain is up to 60 units.

7. (Amended) The additive of ~~any one of claim 1 to 6~~ claim 1, wherein the polymer has the molecular structure:



wherein M in each occurrence independently is hydrogen or  $-\text{[CH}_2\text{-CHR-O]}_n\text{-CH}_3$  with R being  $\text{CH}_3$  or  $\text{CH}_2\text{-CH}_3$  or hydrogen, with the proviso that at least some of the radicals M have



CLAIMS SHOWING AMENDMENTS OF: FEBRUARY 13, 2001

PAGE 2

the meaning of  $-\text{[CH}_2\text{-CHR-O]}_n\text{-CH}_3$ , n is from 3 to 70, ~~preferably greater than 4 and less than 60,~~ and x and y each independently are from 1 to 100.

8. The additive of claim 3, wherein the residual maleic anhydride groups in the polymer are hydrolyzed.

9. A wellbore drilling or service fluid when brought into contact with subterranean clayey formations, said fluid comprising a polymer for stabilizing the clayey formations based on an olefinically unsaturated hydrocarbon with alkylene oxide based side chains.

10. The wellbore fluid of claim 9, being water based.

11. Use of a polymer based on an olefinically unsaturated hydrocarbon with alkylene oxide based side chains for stabilizing shale or clayey formations.

12. A method of stabilizing shale in a subterranean formation comprising the step of injecting an additive into the formation comprising a polymer based on an olefinically unsaturated hydrocarbon with alkylene oxide based side chains.

13. The method of claim 12 wherein the polymer is a copolymer of an olefinically unsaturated hydrocarbon and an ethylenically unsaturated carboxylic acid, carboxylic acid salt or carboxylic acid anhydride with alkylene oxide based side chains.

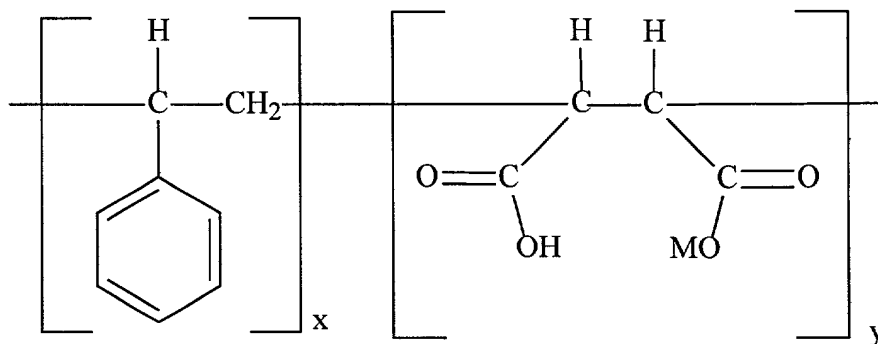
14. (Amended) The method of claim 12 ~~or 13~~, wherein the polymer is a copolymer of styrene derivative and maleic anhydride with alkylene oxide based side chains.

15. (Amended) The method of ~~any one of claim 12 to 14~~ claim 12, wherein the polymer has a molecular weight of from 5000 g / mol to 100,000 g/mol.

16. (Amended) The method of ~~any one of claim 12 to 15~~ claim 12, wherein the weight of the alkylene oxide based side chains is above 200 g/mol.

17. (Amended) The method of ~~any one of claim 12 to 16~~ claim 12, wherein the number of alkoxyates in the polymer side chain is up to 60 units.

18. (Amended) The method of ~~any one of claims 12 to 17~~ claim 12, wherein the polymer has the molecular structure:



wherein M in each occurrence independently is hydrogen or  $-\text{[CH}_2\text{-CHR-O]}_n\text{-CH}_3$  with R being CH<sub>3</sub> or CH<sub>2</sub>-CH<sub>3</sub> or hydrogen, with the proviso that at least some of the radicals M have the meaning of  $-\text{[CH}_2\text{-CHR-O]}_n\text{-CH}_3$ , n is from 3 to 70, ~~preferably greater than 4 and less than 60~~, and x and y each independently are from 1 to 100.

19. The method of claim 14, wherein the residual maleic anhydride groups in the polymer are hydrolyzed.

20. The method of claim 12 wherein the additive is added to a wellbore drilling or service fluid.

21. The method of claim 20 wherein the wellbore fluid is water based.

Shale-Stabilizing Additives

This invention concerns drilling or completion fluids, particularly water-based drilling or completion fluids. More specifically, it pertains to additives for such fluids. Even more specifically, the invention relates to additives used to prevent shales or clayey formations from adversely affecting well drilling or well completion operations.

## BACKGROUND OF THE INVENTION

Drilling fluids are used in well drilling operations, e.g., during drilling of oil and gas wells. During drilling, drilling fluid is pumped down a drillstring, discharged through ports in the drill bit and returned to the surface via the annulus between the drillpipe and the surrounding formation. The drilling fluid performs a variety of functions including cooling and lubricating the drill bit and drillstring, removing rock cuttings generated during the drilling process and carrying them to the surface, suspending cuttings in the annulus when pumping stops, preventing squeezing in or caving of the formation and keeping formation fluids at bay.

Drilling fluids generally comprise a carrier, a weighting agent and chemical additives. Drilling fluids fall into two main categories: water-based drilling fluids, also known as water based muds (WBMs), in which the carrier is an aqueous medium; and oil-based drilling fluids, also known as oil-based muds (OBMs), in which the carrier is oil or a water/oil emulsion. Oil based muds are technically superior to WBMs in certain important respects, including the comparative lack of adverse reactivity of OBMs with shales, one of the most commonly encountered rock types during drilling for oil and gas. The use of OBMs, however, has the disadvantage of resulting in production of large quantities of oil-contaminated waste products such as cuttings that are difficult to dispose of in an environmentally

5 acceptable way. While the use of WBM is environmentally more  
acceptable than of OBMs, the performance of WBM, particularly  
10 when drilling through water sensitive rocks such as shales, is  
technically inferior to that of OBM. Shales exhibit great  
5 affinity for water, and adsorption of water by shales causes the  
shale to swell and produces chemical changes in the rock which  
15 produce stresses that weaken the formation, possibly leading to  
erosion of the borehole or loss of structure. This can lead to  
drilling problems such as wellbore erosion or stuck pipe. In  
10 addition, inferior wellbore quality may hinder logging and  
completion operations.

20 Much effort has been put into improving the performance of WBM  
relative to shales, namely improving the level of so called  
15 shale inhibition of WBM. Various chemical additives have been  
incorporated in WBM in attempts to improve shale inhibition. In  
particular water soluble glycols, polyhydric alcohols (i.e.  
chemicals containing more than one hydroxyl group) or  
polyglycols (i.e. chemicals made using alkylene oxides such as  
20 ethylene oxide or propylene oxide) are widely used for this  
purpose, typically being added to WBM in amounts in the range 3  
to 10% by weight. These chemicals can be collectively referred  
to as Polyols. Polyols used in this way include, for example,  
35 glycerols, polyglycerols, glycols, polyalkylene glycols (PAG),  
eg polyethylene glycols (PEG), polypropylene glycols (PPG) and  
25 copolymers of ethylene and propylene glycols, alcohol  
ethoxylates (AET) and glycol ethers. A typical inhibitive AET is  
an n-butanol derivative of ethylene oxide. The PAGs can have a  
range of ethylene oxide: propylene oxide (EO:PO) ratios and can  
30 be random or block copolymers; a frequently used material of  
this type is understood to be a random copolymer with an EO:PO  
ratio of about 1:1.

45 Variants of polyalkylene glycols and alcohol alkoxylates are for  
35 example described in the International Patent Applications  
WO-96/24645 and WO-96/24646. Others are found in the European  
50 Patent Application EP-A-0495579, the United States Patents

US-A-4830765 and US-A-4172800.

A further source relating to the background of the invention is the Society of Petroleum Engineers Reports SPE 28960 (Mechanism of Shale Inhibition by Polyols in Water Based Drilling Fluids) proposing a credible mechanism that adequately describes how such polyols provide shale inhibition.

Copolymers of styrene and maleic anhydride and a number of derivatives are described for example in the United States Patent No. 3,332,872, for use as viscosity control agents. Hydrophilic-hydrophobic graft copolymers with polystyrene side chains for drilling fluids appear in the United States Patent No. 4,085,168. Other hydrophobically modified polymers based on polyacrylamide and hydroxyethylcellulose have been disclosed for example in the United States Patent Nos. 5,597,783 and 5,637,556.

Shale swelling is considered as a problem not only in the oil field industry. It is encountered as clay swelling in the mining industry, where this phenomenon causes severe difficulties when dewatering the mineral tailings.

In view of the above, it is an object of the invention to provide a novel additive for inhibiting shale swelling. It is another, more specific object of the invention to provide an additive for a WBM.

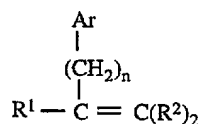
#### SUMMARY OF THE INVENTION

The objects of the invention are achieved by shale-stabilizing additives as set forth in the appended independent claims. According to a first aspect of the invention, there is provided a shale-stabilizing additive comprising a polymer based on an olefinically unsaturated hydrocarbon with alkylene oxide based side chains.

Useful olefinically unsaturated hydrocarbons generally are aliphatic olefinically unsaturated hydrocarbons or vinylidene aromatic monomers.

Aliphatic olefinically unsaturated hydrocarbons include, for example,  $\alpha$ -olefin monomers containing from 2 to 28, preferably from 4 to 20, more preferably from 8 to 18 carbon atoms.

Preferred olefinically unsaturated hydrocarbons are vinylidene aromatic monomers. Suitable vinylidene aromatic monomers include, for example, those represented by the following formula:



wherein  $\text{R}^1$  is hydrogen or an alkyl group containing 1 to 4 carbon atoms, preferably hydrogen or methyl; each  $\text{R}^2$  is independently hydrogen or an alkyl group containing 1 to 4 carbon atoms, preferably hydrogen or methyl; Ar is a phenyl group or a phenyl group substituted with 1 to 5  $\text{C}_1$ - $\text{C}_4$ -alkyl substituents; and n has a value from zero to 4, preferably from zero to 2, most preferably zero. Preferred monomers are styrene or styrene derivatives including  $\alpha$ -methyl styrene, the  $\text{C}_1$ - $\text{C}_4$ -alkyl- or phenyl-ring substituted derivatives of styrene, such as ortho-, meta-, and para-methylstyrene, para-vinyl toluene or mixtures thereof. The most preferred vinylidene aromatic monomer is styrene.

The polymer is preferably a copolymer of an above-described olefinically unsaturated hydrocarbon and an ethylenically unsaturated carboxylic acid, carboxylic acid salt or carboxylic acid anhydride with alkylene oxide based side chains. Preferred olefinically unsaturated carboxylic acids contain 2 to 12, more preferably 2 to 6, carbon atoms in addition to the carboxyl group(s). They are preferably monocarboxylic acids or,

more preferably, dicarboxylic acids. Preferred examples thereof are acrylic acid, methacrylic acid, fumaric acid, maleic acid, the salts thereof, or maleic anhydride. Most preferably, maleic acid, maleic anhydride and/or a maleic acid salt is incorporated in the polymer. The alkali metal salts, particularly the sodium salt, are the preferred carboxylic acid salts.

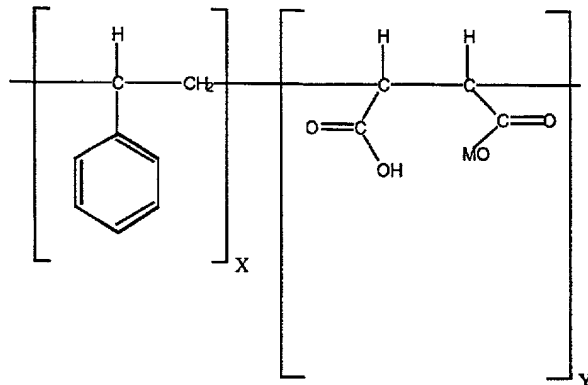
Alkylene oxide based side chains can be introduced into the polymer by esterification of carboxylic groups or anhydride groups with a polyoxyalkylated compound, such as a polyoxyalkylated alcohol. The esterification step can be carried out before or after the polymerization reaction of the dicarboxylic acid (salt) or the anhydride with the vinylidene aromatic monomer. The polymerization reaction and the esterification step are generally known in the art. Preferably 2 to 75 percent, more preferably 20 to 60 percent, most preferably about 50 percent of the total number of carboxyl carbon atoms in the polymer are esterified.

In a preferred embodiment of the invention, the polymer is a copolymer of styrene or a styrene derivative and maleic anhydride with alkylene oxide based side chains.

The molecular weight of the additive is preferably from 5000 g/mol to 100,000 g/mol, more preferably from 10,000 g/mol to 30,000 g/mol. The preferred weight of the alkylene oxide based side chain in accordance with the invention is above 200 g/mol and below 1500 g/mol, more preferably 300-600 g/mol.

The number of alkoxyate groups, e.g.  $-\text{CH}_2-\text{CHR}-\text{O}-$  with R being H,  $\text{CH}_3$  or  $\text{CH}_2-\text{CH}_3$ , per side chain is preferably up to 60 units.

A preferred molecule in accordance with the invention has the molecular structure:



M in each occurrence independently is hydrogen or  $-\text{[CH}_2\text{-CHR-O-]}_n\text{-CH}_3$ , with R being  $\text{CH}_3$  or  $\text{CH}_2\text{-CH}_3$  or, preferably, hydrogen, with the proviso that at least some of the radicals M have the meaning of  $-\text{[CH}_2\text{-CHR-O-]}_n\text{-CH}_3$ . X and Y each independently are from 1 to 100. The total of X and Y should generally be greater than 4 and the invention works best if the total of X and Y is greater than 50. The ratio of X : Y is preferably from 1 : 3 to 3 : 1, more preferably about 1 : 1. The value of n is from 3 to 70, preferably greater than 4 and less than 60. More preferably, n is 7-25.

The above-described polymer is preferably used as an additive in water-based drilling fluids (WBM) or completion fluids or in dewatering operations for mineral tailings.

In another aspect, the invention concerns a drilling fluid with 0.1 to 10 weight per cent (wt%) of the polymer as characterized before. More preferably, the polymer are used at 2 to 7 wt%.

The additives in accordance with the invention provide higher levels of shale swelling inhibition in the presence of weakly hydrated cations, such as potassium, cesium, and ammonium. Inhibition can be obtained solely from using the additives in freshwater or preferably in combination with salts containing for example sodium, calcium, magnesium, or potassium ions.



It can also be expected that the novel additives can improve current methods of dewatering mineral tailings in the mining industry, as today this process is severely hampered by clay swelling.

These and other features of the invention, preferred embodiments and variants thereof, and further advantages of the invention will become appreciated and understood by those skilled in the art from the detailed description following below.

#### EXAMPLE(S) FOR CARRYING OUT THE INVENTION

- The preparation of the chemicals compounds used in the following examples as additives is known. Following the preparation steps laid out for example by H. Dérand et al. in *Macromolecules* 29 (1996), 8770-8775 and by A. Eckert and S.E. Weber in *Macromolecules* 29 (1996), 560-567, copolymers of styrene and maleic acid (SMACs) can be grafted with poly(ethylene glycol) (PEGs) or derivatives, thereof.

The shale inhibition capabilities of additives can be assessed by a number of laboratory techniques such as cuttings dispersion, cuttings hardness and shale swelling tests. These tests are suitable for rapid screening of new additives and are widely used in the industry.

Shale recovery from bottle rolling tests have been used to measure the shale inhibition properties. Tests were done using Oxford Clay cuttings (a water sensitive shale) sieved to 2 - 4 mm. Briefly, the test is a modification of a standard oilfield cuttings dispersion test and consists of adding 10 g of test substrate (Oxford Clay) with 100 ml of test fluid in a 300 ml bottle. The test samples are rolled at 50 rpm for 4 hours. This encourages breakdown and dispersion of the cuttings if they become soft due to interaction with the test fluid. The shale

cuttings are sieved through a 250 micron screen and the amount of shale recovered is measured after drying in an oven. The poly(ethylene glycol) (PEG) used in these tests had a molecular weight of about 600 g/mol.

Bottle rolling tests were done with 5 % w/v solutions of the invention in 7.6 % (Table 1) and 12.9 % w/w KCl (Table 2). The grafted copolymer used in both of these cases was the same. The backbone consisted of an alternating copolymer of styrene and maleic anhydride (SMAC) with grafted poly(ethylene glycol) monomethyl ethers (MPEG 500) side chains of about 500 g/mol. A significant increase in the amount of shale recovered was observed when the invention was used over that of PEG / KCl. A comparison of the results of Table 1 and 2 shows that the amount of shale recovered by the invention increased with the amount of KCl.

TABLE 1. Shale recovery results from bottle rolling tests with Oxford clay cuttings for polyglycol and SMAC grafted copolymer in 7.6 % w/w KCl.

Sample	% Shale Recovery
-----	-----
7.6 % KCl	20
PEG	39
SMAC (MPEG 500)	64

TABLE 2. Shale recovery results from bottle rolling tests with Oxford clay cuttings for PEG and SMAC copolymer with MPEG 500 grafts in 12.9 % w/w KCl.

Sample	% Shale Recovery
-----	-----
12.9 % KCl	29
PEG	51
SMAC (MPEG 500)	91

The amount of shale recovery of the invention as a function of the grafted MPEG chain length is shown in Table 3. The results show that all MPEG variations of the invention show improved shale recovery compared to that of polyethylene oxide and that the best results are obtained for copolymers with MPEG grafts with molecular weight of about 300 to 400 g/mol.

TABLE 3. Shale recovery results from bottle rolling tests with Oxford clay cuttings for polyglycol and grafted copolymer in 7.6 % w/w KCl where the molecular weight of graft polyethylene oxide varies from 200 to 1500 g/mol.

Sample	% Shale Recovery
-----	-----
15 7.6 % KCl only	25
25 PEG	38
SMAC MPEG 200	54
SMAC MPEG 300	87
SMAC MPEG 400	85
20 SMAC MPEG 500	72
SMAC MPEG 600	69
SMAC MPEG 750	70
SMAC MPEG 1100	66
SMAC MPEG 1500	49

Table 4 shows bottle rolling test results in 12.9 % w/w KCl that include a polymer that consists of a backbone with 2 styrene units for every maleic anhydride unit. MPEG 500 was used as the grafting polymer. The results show that increasing the amount of styrene in the backbone increased the amount of shale recovered.

TABLE 4. Shale recovery results from bottle rolling tests with Oxford clay cuttings for polyglycol and grafted copolymer in 12.9 % w/w KCl. The backbone of SMAC 2:1 Styrene MPEG 500 was composed of 2 styrene units for every maleic anhydride. The grafts consisted of MPEG 500.

Sample	% Shale Recovery
-----	-----

12.9 % KCl	27
PEG	53
SMAC MPEG 500	85
SMAC 2:1 Styrene MPEG 500	95

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The effect of drilling fluid additives on reactive shales can also be assessed by the Hassler Cell test. Briefly, fluids are pumped through a confined Oxford Clay core perpendicular to the bedding planes at high pressure and the permeability of the core to the test fluid is measured and compared with that of a synthetic pore fluid. In general, greater shale inhibition can be achieved by reducing the permeability of the test fluid within the core. For instance, the permeability of oil based muds (OBM) is much lower than the pore fluid due, in part, to the change in wettability caused by OBM surfactants. Inhibitive water based drilling fluids also show significant reductions in fluid permeability. PEG / KCl based fluids show permeability reductions from 11 to 46 % and silicate based systems show reductions of between 65 - 80 %. The permeability reduction caused by the invention (SMAC MPEG 500) was about 96.9 %. This is the greatest amount of reduction for a water based fluid observed to date and is equal to that of an oil based drilling fluid.

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TABLE 5. Flow Rate Changes in Oxford Clay Cores by Various Fluids in Hassler Cell Tests.

Fluid type	Flow Rate before [g/hr]	Flow Rate after [g/hr]	% Original Rate
-----	-----	-----	-----
10 % KCl	0.043	0.061	142
PEG / KCl	0.037	0.033	89
PEG-C <sub>6</sub> H <sub>6</sub> / KCl	0.037	0.020	54
KCl / Silicate	0.052	0.010	19
NaCl then			
KCl / Silicate	0.068	0.024	35
70:30 OBM	0.036	0.0024	6.6

SMAC (MPEG 500) / KCl      0.1397      0.0043      3.1

Improved shale inhibition is exhibited by many variations of the invention as is shown above. The improved shale inhibition is primarily the result of the hydrophobic portions of the molecule and inhibition increases with the amount of styrene in the backbone. The invention appears to provide shale inhibition by reducing the permeability of aqueous solutions in reactive shales.

The invention also shows improved results in bulk cuttings hardness test which is a modification of a standard industry analysis. In this experiment 30 g of sieved Oxford Clay cuttings (2-4 mm) were put in 200 mls of the test fluid for 2 hours. The test fluid is drained off and the cuttings are put into a press cell. The cuttings are then pressed through a plate with holes and the amount of torque required is measured with every turn of the torque gauge. The plateau torque is quoted as the cuttings hardness. Table 6 shows the results of tests conducted on a series of test samples in 12.9 % KCl. PEG and SMAC MPEG 500 samples contained 5 % w/v test additive.

TABLE 6. Bulk Cuttings hardness in 12.9 % KCl fluids.

Sample	Cuttings Hardness [N*m]
-----	-----
12.9 % KCl	1.6
PEG	8
SMAC MPEG 500	12
natural Oxford Clay (no fluid)	14

The results in Table 6 show that the MPEG grafted copolymers results in harder cuttings than the polyethylene glycol / KCl mud.

The results of clay dispersion, Hassler Cell and cuttings hardness tests clearly show the improved levels of inhibition

provided by fluids containing MPEG grafted SMAC copolymer in place of poly(alkylene oxides) in KCl based fluids.

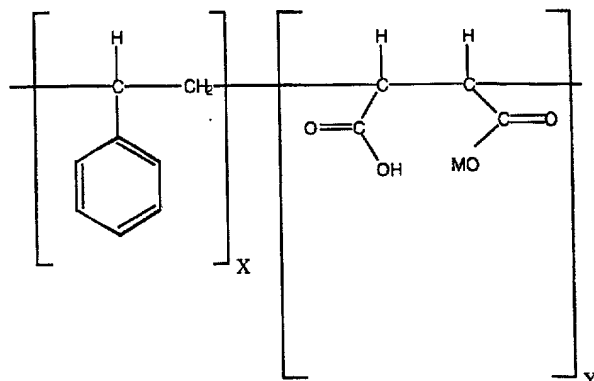
The performance of the KCl / SMAC system was measured as a function of the KCl concentration, SMAC concentration and fluid conditions. The performance was found to increase with the concentration of KCl and SMAC up to a threshold value after which performance levelled. Tests conducted with Oxford clay found that the threshold concentration of KCl to be between 10 and 14 % w/w. The threshold value for maximum performance of SMAC was between 1 and 2 % w/v.

SMAC performance increased substantially if residual maleic anhydride groups present were hydrolysed to the acid form. SMAC with maleic acid groups are sensitive to the pH of the fluid. The optimum shale recovery was found to occur at pH of 9. Excellent performance was observed for SMAC fluids in the pH range of 7 to 11. Shale inhibition declined rapidly above pH of 11.5

Replacement of the polyethylene glycol side chains with polypropylene glycol based side chains gave inferior results.

## CLAIMS

1. A shale-stabilizing additive comprising a polymer based on an olefinically unsaturated hydrocarbon with alkylene oxide based side chains added to a wellbore drilling or service fluid to be injected into subterranean formations.
2. The additive of Claim 1 wherein the polymer is a copolymer of an olefinically unsaturated hydrocarbon and an ethylenically unsaturated carboxylic acid, carboxylic acid salt or carboxylic acid anhydride with alkylene oxide based side chains.
3. The additive of claim 1 or 2, wherein the polymer is a copolymer of styrene or a styrene derivative and maleic anhydride with alkylene oxide based side chains.
4. The additive of any one of claims 1 to 3, wherein the polymer has a molecular weight of from 5000 g/mol to 100,000 g/mol.
5. The additive of any one of claims 1 to 4, wherein the weight of the alkylene oxide based side chains is above 200 g/mol.
6. The additive of any one of claims 1 to 5, wherein the number of alkoxyates in the polymer side chain is up to 60 units.
7. The additive of any one of claims 1 to 6, wherein the polymer has the molecular structure:



wherein M in each occurrence independently is hydrogen or -  
 $[\text{CH}_2\text{-CHR-O-}]_n\text{-CH}_2$  with R being  $\text{CH}_3$  or  $\text{CH}_2\text{-CH}_3$  or hydrogen,  
 with the proviso that at least some of the radicals M have  
 the meaning of  $-\text{[CH}_2\text{-CHR-O-}]_n\text{-CH}_2$ , n is from 3 to 70,  
 preferably greater than 4 and less than 60, and X and Y  
 each independently are from 1 to 100.

8. The additive of claim 3, wherein the residual maleic anhydride groups in the polymer are hydrolyzed.
9. Wellbore drilling or service fluid, said fluid comprising a polymer based on an olefinically unsaturated hydrocarbon with alkylene oxide based side chains to be brought into contact with subterranean, specifically clayey formations.
10. The wellbore fluid of claim 9, being water based.
11. Use of a polymer based on an olefinically unsaturated hydrocarbon with alkylene oxide based side chains for stabilizing shale or clayey formations.



**DECLARATION FOR PATENT APPLICATION AND  
POWER OF ATTORNEY**

As a below named inventor, I hereby declare that:

My residence, Mailing address and citizenship are as stated below next to my name,

I (we) believe we are the original, first and joint inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled

**SHALE-STABILIZING ADDITIVES**

the specification of which

(Check one) ☐ is attached hereto.

☒ was filed on February 15, 2001 as

Application Serial No. 09/763,239

and was amended February 15, 2001  
(if applicable)

I (we) hereby state that we have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I (we) acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

☒ I (we) hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s):

			<u>Priority Claimed</u>	
<u>PCT/GB99/02623</u>	<u>GB</u>	<u>09 August 1999</u>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	Yes	No
<u>9817780.1</u>	<u>GB</u>	<u>15 August 1998</u>	<input checked="" type="checkbox"/>	<input type="checkbox"/>
(Number)	(Country)	(Day/Month/Year Filed)	Yes	No

☒ I (we) hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I (we) acknowledge the duty to disclose

material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

PCT/GB99/02623 (Application Serial No.)	09 August 1999 (Filing Date)	Pending (Status) (Patented, Pending, Abandoned)
 (Application Serial No.)	 (Filing Date)	 (Status) (Patented, Pending, Abandoned)
 (Application Serial No.)	 (Filing Date)	 (Status) (Patented, Pending, Abandoned)
 (Application Serial No.)	 (Filing Date)	 (Status) (Patented, Pending, Abandoned)

I (we) hereby appoint the following as our representative(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith: **STEPHEN H. CAGLE**, Attorney (Reg. No. 26,445), **PATRICIA A. KAMMERER**, Attorney (Reg. No. 29,775), **CRAIG M. LUNDELL**, Attorney (Reg. No. 30,284), **JANELLE D. WAACK**, Attorney (Reg. No. 36,300), **CARTER J. WHITE**, Agent (Reg. No. 41,374), and **ROBERT P. AUERBACH**, Agent (Reg. No. 46,525) each an attorney or agent with the law firm of HOWREY, SIMON, ARNOLD, & WHITE, LLP as its attorney or agent so long as they remain with such law firm.

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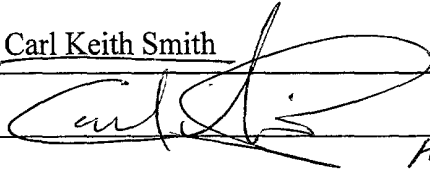
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I (we) hereby declare that all statements made herein of our own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under §1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full name of first inventor Carl Keith Smith

First Inventor's signature



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